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博 士 学 位 论 文

直接甲醇燃料电池阻醇质子交换膜制备、表征及其质子/甲醇传输机理研究

Synthesis, Characterization and Proton/Methanol Transport Mechanism of Methanol-blocking Proton Exchange Membrane for Direct methanol Fuel Cell (DMFC)

李　涛

指导教师姓名：杨　勇　教授
专 业 名 称：物 理 化 学
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摘　要

直接甲醇燃料电池（DMFC），其燃料甲醇常温下为液体，储存和运输较为便利和安全，并且具有高的能量密度；因其直接氧化甲醇，电池系统较为简单和易于小型化。因此直接甲醇燃料电池作为新一代高效电源在便携式电子设备、电动车上具有良好的应用前景。作为直接甲醇燃料电池关键组件之一的质子交换膜，目前广泛使用的是全氟磺酸膜，如杜邦公司生产的 Nafion 系列产品。这种材料具有优异的化学及热稳定性，并且当其充分润湿时表现出优秀的质子电导率。但是全氟磺酸膜也存在着燃料甲醇从阳极向阴极渗透严重的问题，甲醇渗透不但浪费燃料（因渗透造成得浪费率最多可达 40%），而且会在阴极造成混合电位并毒化阴极催化剂，从而大大降低了燃料电池的性能，因此甲醇渗透成为阻碍直接甲醇燃料电池实际应用的主要问题之一。

要改进现有质子交换膜的性能，就必须深入了解质子交换膜中甲醇传输的机制以及影响甲醇传输的各项主要因素。基于以上研究目标，本论文对现有全氟磺酸膜进行了复合改性以降低其甲醇渗透率，尝试制备了几种新型部分氟化型复合聚合物膜体系，并对质子交换膜的结构、阻醇性能及其可能的物质传输机理进行了研究，取得的主要结果如下：

1．硅氧化物表面不同基团调控全氟磺酸质子交换膜性能的研究

论文选用了具有极性较强的相对亲水有机基团的硅烷偶联剂，制备了一系列 Nafion/有机硅氧化物复合膜。发现当复合膜中所含的硅氧化物量基本相同时，使用有机基团中含有氨基的硅烷偶联剂改性的复合膜表现出极低的甲醇渗透率及质子电导率。在此基础上还发现，当改变与-NH_2 相连的基团的电负性时，可以对生成的复合膜的甲醇渗透率及质子电导率进行调控。如利用带有脲基的有机硅烷偶联剂改性的复合膜与 Nafion117 膜相比，甲醇渗透率降低了 89%，而质子电导率仅下降了 49%；并且表现出比 Nafion117 更稳定的电池性能。实验结果表明为降低全氟磺酸膜的甲醇渗透率，应从甲醇的渗透通路——膜内部互相连接的离子簇入手。而离子簇是由磺酸基团充分水合并集聚形成的，因此利用与磺酸基团有相互作用的添加剂可以影响离子簇的形成，从而抑制甲醇的渗

透，但由于质子传导也必须经由相互连接的离子簇，所以这种影响同时降低了膜的质子电导，对膜的综合性能的提高产生了不利影响。

2．半互贯穿网络型(semi-IPN)Nafion/PVP(聚乙烯吡咯烷酮)复合膜的性能研究。

通过对 Nafion/有机硅氧化物复合膜的研究发现，所得复合膜的甲醇渗透率的降低总是以牺牲其质子电导率为代价的。这可能是由于在磺酸化质子交换膜中甲醇与质子有着近似的传输路径，因而很难提高此类膜对质子的选择透过性。而互贯穿聚合物网络膜(IPN)由两种或多种相互独立的交联聚合物构成，通过调节各种聚合物的比例、交联程度、交联结构有可能获得高质子选择性的质子交换膜。

本论文选择 4,4’－双叠氮蒀－2,2’二磺酸钠（DAS）为交联试剂，以紫外光引发，使聚乙烯吡咯烷酮（PVP）在 Nafion 膜中发生交联，从而制备了 semi-IPN 型 Nafion/PVP 复合膜。对复合膜的性能测试发现，PVP 含量不同的复合膜，均表现出较低的甲醇渗透率（为 Nafion117 的 41~47%），而 PVP 含量较少的复合膜表现出比 Nafion117 更高的室温质子电导率（最多可增加～30%），并且复合膜还表现出比 Nafion117 膜更佳的热稳定性，其氟醚支链的分解温度提高了近 60 度。通过对复合膜广角 X 射线衍射及 1H 固体核磁共振谱的表征，认为这是因为网状的交联 PVP 结构限制了 Nafion 分子链的自由蠕动，影响了全氟磺酸膜充分水合时内部离子簇的相互连接，从而抑制了甲醇渗透；而质子具有通过氢键的跃迁传输机制，交联试剂的引入同时增加了复合膜中磺酸基团的密度，所以特定交联度的复合膜表现出更高的质子电导。研究结果表明，利用质子相对于甲醇所独有的跃迁传输机制，可能设计出质子选择性更优的高性能质子交换膜。

3．互贯穿网络型(IPN)聚偏氟乙烯(PVDF)/2-丙烯酰胺基-2-甲基丙磺酸(AMPS)复合聚合物质子交换膜。

针对目前全氟磺酸质子交换膜价格昂贵的问题，并为了进一步研究 IPN 型质子交换膜的特性，本论文还开展了 IPN 型部分氟化复合聚合物质子交换膜的研究。合成了以聚偏氟乙烯(PVDF)为阻醇聚合物及质子交换膜聚合物骨架，以 2-丙烯酰胺基-2-甲基丙磺酸(AMPS)为离子交换载体（以乙烯基三乙氧基硅烷(VTES)、二乙烯基苯(DVB)、N ,N′ - 亚甲基双丙烯酰胺(NMBA)等对 AMPS 进

行交联）的 IPN 型 PVDF/AMPS 质子交换膜。通过对 AMPS 的预聚合，选择合适的交联试剂及用量，优化交联反应时间和温度等措施，使制备的质子交换膜具有良好的机械性能，与 Nafion117 相比甲醇渗透率降低了 2/3，质子电导率基本不变，质子选择系数可达 Nafion117 膜的 2.5 倍。同时发现，相对于离子聚合物中离子交换位（磺酸基团密度）的多少，膜的交联程度、微观结构及表面形貌对质子交换膜的性能影响更大。在此基础上，我们对 PVDF/AMPS 质子交换膜进行了紫外接枝 AMPS 的表面修饰，实验结果发现，表面改性可进一步提高质子交换膜的质子电导，使膜的质子选择系数达到 Nafion117 膜的～3.0 倍。

关键词：直接甲醇燃料电池、质子交换膜、甲醇渗透率、质子电导率、复合膜、氨基、互贯穿聚合物网络、部分氟化质子交换膜、交联

Abstract

The direct methanol fuel cell (DMFC) is a promising power source candidate for portable electronic devices and electric vehicles due to its high energy efficiency and environmental compatibility. Its fuel, methanol, which is liquid at room temperature, can be easily and safely stored and transported. In addition, the DMFC system is simple in design and can be operated without fuel reforming. So far, the perfluorosulfonic acid (PFSA) membrane (e.g. Nafion by Dupont) has been used widely as proton exchange membrane (PEM) for the DMFC, owing to its excellent stability both in chemical and thermal environment, as well as its high proton conductivity when contains enough water. However the main disadvantage of PFSA membrane is methanol crossover, and over 40% of methanol could across the membrane at most. Methanol crossover causes loss of fuel, reduced cathode voltage and cell performance. Such disadvantage is also one of the major problems in DMFC application.

In order to improve the performance of the existing PEM, it's important to understand the methanol crossover mechanism and the effects of PEM properties on the methanol transport in PEM. Therefore, the thesis mainly concentrated on modifying the PFSA membrane to lower its methanol permeability, trying to design partial fluorizated PEM candidate, as well as investigating the structure, the methanol-blocking performance, methanol and proton transport mechanism of the PEM. The main results of the thesis are as follows:

1. The effects of organic silica bearing different organic groups on the performances of the Nafion/organic silica composite membranes.

A series of Nafion/organic silica hybrid membranes has been prepared by using organic silane coupling agents (SCA) bearing different hydrophilic functional groups. With approximate silica content, the composite membrane modified by SCA bearing aliphatic amino groups (SILCPM3) was found to exhibit extremely low proton conductivity and methanol permeability compared with other composite membranes.

Moreover, by controlling the electronegativity of the group connected to the amino group, the methanol permeability and proton conductivity of the composite membrane could also be adjusted. E.g. the composite membrane modified by SCA bearing urea group was found to exhibit 89% lower methanol permeability, 49% lower proton conductivity, as well as improved cell performance compared with Nafion117 membrane. The results showed that, in order to decrease methanol crossover in the films, we should modify the PFSA membrane aiming at the methanol transfer path (the connected ion clusters formed by terminal $-SO_3H$ groups). Thus the additive which has interaction with sulfonic group could also affect the formation of ion clusters, and restricts the methanol permeability as well. However, proton transportation also involves in the connected clusters, the effect of additive on sulfonic group may also depress the proton conductivity, and worsen the cell performance of the composite membranes.

2. The study of Nafion/cross-linked PVP semi-interpenetrating polymer network (IPN) membrane.

From the study of Nafion/organic silica composite membranes, it can be seen that the transfer of proton and methanol decreases simultaneously under modifying. This suggests that protons and methanol have similar molecular transport mechanisms in sulfonic acid containing PEMs, which makes it difficult to improve selectivity for the DMFC application. Interpenetrating polymer networks (IPNs) consists of two independent cross-linked polymer, the IPNs may obtain high selectivity in theory by adjusting the structure, the molar ratio, and the cross-linking degree of the two polymers.

The thesis chose 4, 4’-diazostilbene-2, 2’-disulfonic acid disodium salt (DAS) as cross-linking agent to crosslink poly(vinyl pyrrolidone) (PVP) in commercial Nafion117 membranes under the irradiation of ultraviolet. The semi-IPN Nafion/PVP membranes exhibited decreasing methanol permeability with the increasing of the content of PVP. However, with appropriate amount of PVP, the semi-IPN membrane showed even higher proton conductivity than Naifon117(~30%

higher). It was also found that the decomposition temperature of the fluorinated ether side-chain of semi-IPN membranes was 60^{o}C higher than that of Nafion117, which means that the semi-IPN membranes had better thermal stability than pristine Nafion117. From the characterization of wide angle XRD and 1H solid-state NMR spectra, it can be concluded that the introduction of cross-linked PVP network restricted the free squirm of Nafion side-chain, which influenced the hydration of terminal sulfonic acid group and weakened the connection of ion clusters, thus depressed the methanol crossover. Howerver, the extra sulfonic acid groups supplied by crosslinking agent DAS as well as the acid-base interaction produced by amino group and sulfonic acid group strengthened the hopping transfer of proton, thus the semi-IPN membranes exhibited improved proton conductivity with appropriate amount of PVP. Furthermore, the unique Grotthuss transfer mechanism of proton compared with methanol moleculer should be taken into account for designing and synthesizing more suitable proton exchange membrane candidates for DMFC.

3. The preliminary study of PVDF/AMPS interpenetrating polymer network membrane.

Aiming at reducing the cost of PEM, and the further exploration of new IPN membranes with good performance, a novel partial fluorizated PEM candidate was also been prepared. Poly (vinylidene fluoride) (PVDF) was chosen as polymer matrix, 2-acryamido-2- methyl-1-propane sulfonic acid (AMPS) was chosen as ionomer. AMPS was cross-linked by different cross-linking agents (e.g. vinyltriethoxysilane (VTES), divinylbenzene (DVB), and N,N'-Methylenebisacrylamide (NMBA)) to form PVDF/ AMPS IPN membranes. Through the pre-polymerization of AMPS, selecting proper cross-linking agent, as well as optimizing molar ratio, reaction time and temperature, the performance of the PVDF/AMPS IPN membranes had been optimized. Compared with Naifon117, the new membrane exhibited ~2/3 lower methanol permeability but similar proton conductivity, and ~1.5 time higher proton selectivity. It was also found that the cross-linking degree, the micro structure and the surface morphology of the IPN

membranes was more important to proton selectivity than the amount of ionomer. The thesis also tried to do some surface modification of PVDF/AMPS IPN membrane via photoinitiated graft polymerisation with AMPS. The results showed that, after surface modification, the proton selectivity of the new membrane can reach 3 times of that of Naifon117.

Keywords: Direct methanol fuel cell, proton exchange membrane, methanol permeability, proton conductivity, composite membrane, amino group, interpenetrating polymer networks(IPN), partial fluorizated, cross-linking